Organic-inorganic hybrids

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Chapter 2

Properties of Inorganic and Organic Materials

Few people have experience with both organic and inorganic electronic materials. Therefore this chapter gives a short introduction to both fields. This chapter is written at introductory level and is far from complete. More thorough introductions are provided by the references given in this chapter.

2.1 Inorganic Electronics

The inorganic elements are widely used in applications; from concrete and steels in construction works to the silicon in your computer. In general, inorganic materials are mostly used for applications in which robustness and long-life properties are required. Inorganic materials[1] are the basis ingredient for conventional electronics and computers. They are mainly insoluble and have high melting temperatures. Therefore, the processing of inorganic materials for electronic applications is based on thermal evaporation and lithography: techniques that require high-tech equipment.

For electric transport in the electronic devices, metals as copper, aluminum and gold are used. The logic is performed inside the processor (see picture 2.1), which consists of billions of interconnected transistors. These transistors can be compared to an electronic tap: the conduction channel between the "*source"* and "*drain"* can be opened and closed by applying a voltage to the *"gate".* These transistors are built out of a semiconducting material. For this purpose, silicon (Si) is widely used as it can be oxidized to the insulating silicondioxide, which facilitates the fabrication of integrated circuits. On the other hand, memory applications like hard drives are based on the magnetic remanence in ferromagnetic materials as iron oxide.

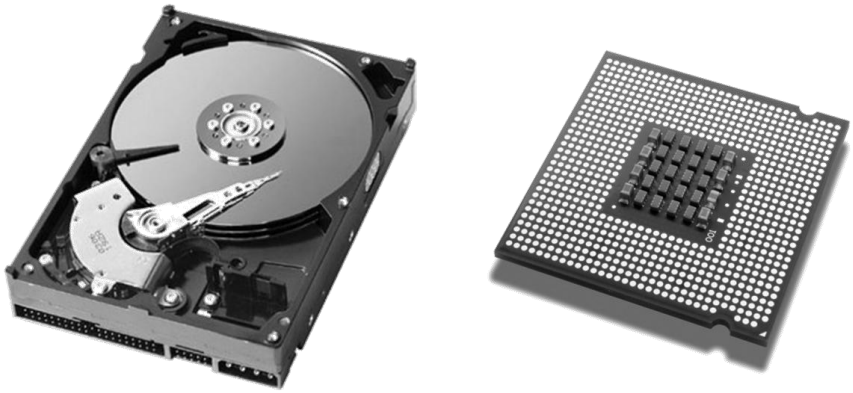

Figure 2.1: Two applications of inorganic materials in electronics. Left, a hard drive that stores data on the basis of magnetism in iron oxide or cobalt-based alloys. Right, a processor that performs calculations based on billions of silicon transistors.

2.1.1 Inorganic Crystals

Crystalline inorganic materials can be regarded as stacks of atoms that are held together by van der Waals, ionic, covalent or metallic interactions.[1, 2] The inorganic components discussed in this thesis are held together by ionic interactions: The transition metal ions are positively charged and the halogens negatively charged. These positive and negative charges attract each other and make the atoms form a lattice below the melting temperature. The atoms can stack in different lattices, depending on their size and chemical nature.[3] An example of a stack of atoms is shown in figure 2.2. In this picture a perovskite structure is shown of $CaTiO_3$[4] in the so called ball and stick model (left) and in the space filling model (right). The latter representation gives a more realistic representation of the electron density but appears less orderly and therefore the ball and stick model is used in this thesis.

Crystals are larger pieces (≥ 1 μm) of material in which the atoms are stacked coherently, in a translational invariant fashion. The smallest repeating building block of the crystal is called the *"unit cell"*. Besides this *"translational symmetry"*, a crystal often possesses many other symmetry operations, such as rotation and mirror symmetry. On the basis of these symmetry characteristics the crystals are classified in a space group.[5]

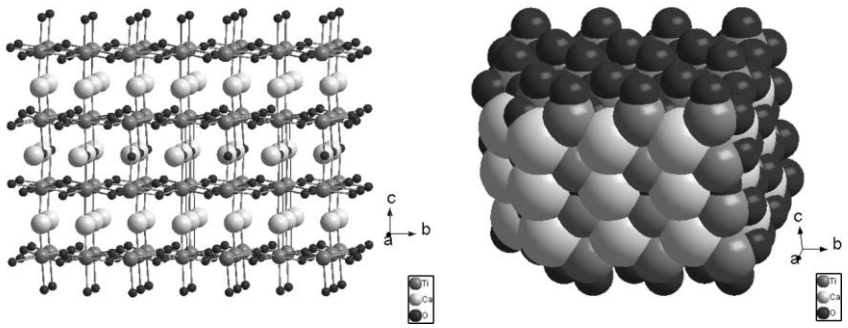

Figure 2.2: The inorganic material $CaTiO_3$ forms a lattice with the perovskite structure. The black spheres represent oxygen, the gray titanium, and the white calcium atoms. The right and the left picture show the same material in a different representation: The left picture is the so called ball and stick model that will be used throughout this thesis. The right picture is the space filling model, which is closer to the actual electron density.

The physical properties of a material are related to the way of stacking of the atoms in the crystal structure, and thus it is very instructive to know the unit cell and the space group of a material. But how is the crystal structure determined? The distance between the atoms is ~3 Å (= $3 \cdot 10^{-10}$ meter). This is much smaller than the wavelength of visible light and thus it is impossible to see even with the best microscope. Therefore we use light with a much shorter wavelength, X-rays, to determine the crystal structure. X-rays are scattered by the electrons that orbit around the atomic nucleii.[6] The X-rays that are scattered by different atoms of the crystal interfere with each other and result in an interference pattern as shown in figure 2.3. The location of the maxima in these interference patterns is described by the condition for constructive interference in Bragg's Law:[3]

$$n\lambda = 2d\sin\theta \qquad (2.1)$$

In which n is an integer number, λ is the wavelength of the X-ray and θ is the angle of the incoming light with respect to the crystallographic scattering plane. The d denotes the distance between two crystallographic planes, see figure 2.3. The intensity of the maxima in the interference pattern reflects the type of atom that is present in the plane.

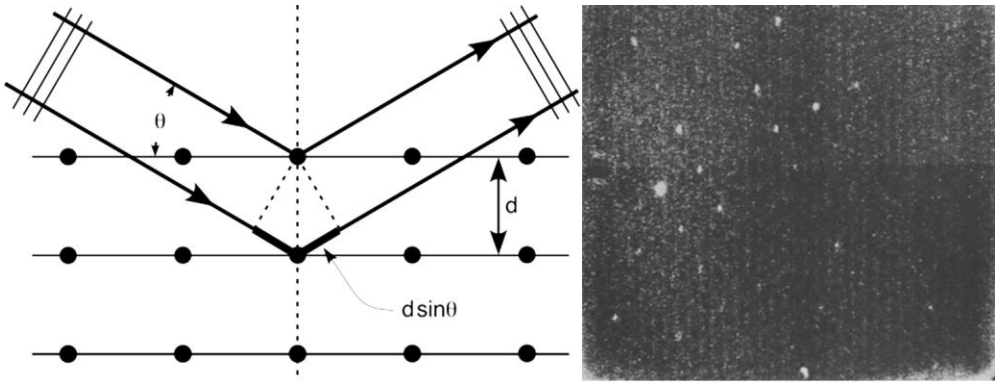

Figure 2.3: Left) A schematic representation of interference by two x-rays in accordance with Braggs Law, see text. The occurrence of constructive interference depends on the incoming angle,θ, and the distance, d, between the crystallographic planes. Right) For single crystals this constructive interference results in an interference pattern. Here, a picture of our Apex detector is shown, on which the interference in a 60°-range of 2θ is projected.

The integrated intensity of the maxima in the interference pattern is the square of scattering amplitude of the crystal, F(Q), which is given by:[7]

$$F(Q) = \sum_{r_j} f_j(Q) e^{iQ \cdot r_j} \sum_{R_n} e^{iQ \cdot R_n} \qquad (2.2)$$

The Q is the scattering vector, and reflects the direction of the incoming and outgoing X-ray beams. The Laue condition indicates that F(Q) is non-zero only if this scattering factor coincides with a reciprocal lattice vector R_n. This statement is identical to the interference condition described by the Bragg's Law (2.1). This Laue condition is reflected in the second term of (2.2). It is a sum over al lattice sites described by the reciprocal lattice vectors; R_n. R_n reflects the translational symmetry of the unit cell in the crystal. This term confines the X-ray scattering to distinct points in reciprocal space, in which $Q=R_n$.

The integrated intensity in each of these points is proportional to the square of the unit cell structure factor that is depicted as the first sum in equation (2.2). This factor consists of information on the type and the positions of atoms in the unit cell. The r_j reflects the atomic positions within the unit cell. The various atomic positions are often related to each other by symmetry operations such as rotations and

mirror planes. On the basis of those symmetry relations, the materials are classified in *spacegroups*. This symmetry within the unit cell can results in a set of reflection conditions on top of the general Laue condition. If all the reflection conditions are fulfilled, the intensity of the peak is determined by the f_j: the atomic structure factors for atoms "j". This value increases with the number of electrons in the atom. In the limit that the scattering vector goes to zero: f_j (Q=0)=Z. (Z is the number of electrons of a particular atom).

To determine the crystal structure, the interference pattern is collected for many different orientations (Q). With the help of sophisticated computer programs[8] and human expertise the crystal structure can be reconstructed from these interference patterns.

2.1.2 Magnetic Properties of Inorganic Materials

All materials are magnetic: high magnetic field research showed that even strawberries and frogs can be levitated on the basis of their magnetic properies.[9] However, not all types of magnetism are suitable for electronic applications. In electronic devices magnetic materials are used e.g. to transmit/store data and transform power. For these applications ferromagnetic materials are most suitable. In magnetic materials the magnetic dipoles are caused by atoms or ions with unpaired electrons that have a magnetic dipole (spin). If the interaction between these magnetic dipoles forces them to align their magnetic moments, the material is called ferromagnetic. In hard drives every bit consists of a group of aligned spins: by turning the spin direction forward or backwards, information is stored. So, for ferromagnetism two ingredients are crucial: 1) the presence of magnetic dipoles and 2) the interaction that forces those dipoles to align their moments.

First, the origin of local magnetic dipoles in transition metals will be discussed. The transition metals are elements with an incomplete d-subshell in the neutral or ionic state. The d-orbitals are the outermost orbitals and their energies are strongly affected by the crystal field, however they have a limited role in the bonding and thus their incomplete d-subshells are maintained inside the crystal lattice. The magnetic moment of the transition metal ion depends on the number of unpaired spins in the d-shell.

As a rule of thumb: the number of electrons in the d-shell of a transition metal is equal to the number of the group minus the oxidation state of the metal ion. For example, the neutral Mn belongs to group 7. In the hybrids, Mn is present as a charged ion Mn^{2+}. Thus the number of electrons in the d-shell is 7-2 = 5. For an isolated ion, the 5 d-orbital are degenerate (they have the same energy), see figure 2.4. The 5 electrons occupy orbitals in accordance with the Hund rules: The electrons prefer to firstly fill each of those degenerate orbitals with one electron, with alignment of the spins.[11] For an isolated Mn^{2+} ion this results in 5 unpaired spins and a spin quantum number of 5 x 1/2 = 5/2. In crystals, the transition metal ions are surrounded by anions, called ligands. In most cases the metal ions are coordinated by 4 or 6 anions that form a tetrahedron or octahedron around the transition metal ion, respectively. Those ligands influence the energy of the d-orbitals in such a way that the degeneracy is partially removed.[12]

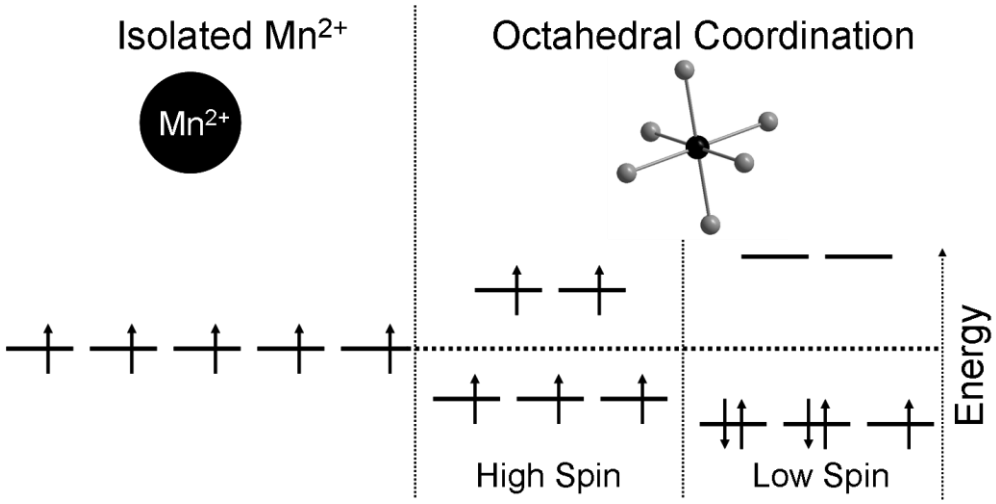

Figure 2.4: A schematic representation of the energy levels of the d-orbitals of the transition metal. For an isolated ion those d-orbitals have the same energy (they are degenerate). The Mn^{2+} has 5 electrons (denoted by the arrows), in these d-orbitals, that each occupies a different orbital, in accordance with the Hund rules. In the octahedral lattice environment, the energy levels split up. The magnitude of this split up is determined by the electron density on the ligands. If this split up is small, the high spin situation of the isolated ion can be maintained. However if the splitting is large, a low spin situation is more favorable.

The way in which the energy levels split-up is determined by the coordination of the ligands and the electronic properties of those ligands. For an octahedron the split-up is shown in figure 2.4: two levels shift up and three shift down in energy with respect to the energy levels of the isolated ions. The magnitude of the energy splitting depends on the type of ligand. If the split-up is small, the high spin situation of the isolated ion can be maintained and the magnetic moment is still 5/2. However, if the splitting is large, a low spin situation is more favorable, in which only one unpaired spin is left. The split-up of the d-orbital energy levels can thus lead to a reduction of the magnetic moment of the ion.

The hybrids that are discussed in this thesis are often based on copper, Cu. The Cu^{2+} has 9 electrons in the d-orbitals and thus has one unpaired spin, regardless of the magnitude of the octahedral splitting. The octahedral coordination is not ideal for this ion. The total energy of the d-electrons can be lowered if the octahedron is slightly distorted: 2 of the 6 metal to ligand bonds are longer than the other 4, see figure 2.5. This distortion is called a Jahn-Teller distortion and results in an additional splitting of the d-orbital energy levels.[13] This distortion does not influence the magnetic moment of the ion, though it can have major impact on the interactions between the magnetic dipoles as will be shown in chapter 4.

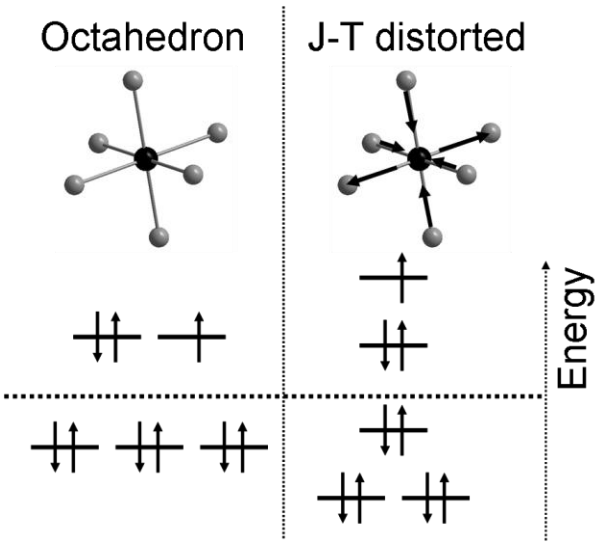

Figure 2.5: A schematic representation of the d-orbital energies for the Cu^{2+} ion in an octahedral environment (left). The Cu^{2+} ion has 9 electrons in the d-orbitals. In this electron configuration a distorted octahedron (right) is energetically more favorable, due to the shift of the filled energy levels to lower energy. This distortion is called the Jahn-Teller effect.[13]

The second ingredient crucial for ferromagnetism is an interaction that forces the magnetic dipoles to align their moments. There are many different interactions possible between the magnetic ions. Here we shortly mention the most common interactions, for further reading we refer to Blundell.[14]

Any set of two magnetic dipoles, μ_1 and μ_2, at a distance r, will have a magnetic dipolar interaction that is given by:

$$E = \frac{\mu_0}{4\pi r^3}[\mu_1 \cdot \mu_2 - \frac{3}{r^2}(\mu_1 \cdot \vec{r})(\mu_2 \cdot \vec{r})] \qquad (2.3)$$

The sign of the interaction depends on the relative orientation of the dipoles: if the directions of the dipole are parallel to r, it will tend to align the dipoles in the same direction and thus the interaction is ferromagnetic. If, however, the directions of the magnetic dipoles are perpendicular to r, it will tend to orient the dipoles in the opposite direction and thus the interaction is antiferromagnetic. In general, these dipole-dipole interactions are relatively small between magnetic ions in a crystal and do not result in ordering temperatures higher than 1 K.

In case of small distances between the magnetic ions, up to 3 Å (= $3 \cdot 10^{-10}$ meter), the orbitals overlap and direct magnetic exchange can occur. Direct exchange is a magnetic interaction due to the direct overlap between the magnetic ions. The sign of the direct exchange interaction depends on the relative orientation of the orbitals and the number of electrons in those outer orbitals.[15]

Many magnetic materials, however, have magnetic interactions that are based on indirect exchange: the magnetic exchange occurs via an intermediate electron or (non-magnetic) ion. In conducting materials, like metals, the magnetic interaction can be mediated by the conduction electron. This interaction is called the RKKY interaction. The sign of this interaction has an oscillatory dependence on the distance between the magnetic ions and it can span a relatively large distance.

The most common magnetic interaction in the $MCl_{3+x}(YNH_3)_{1+x}$ hybrids is an interaction mediated by the non-magnetic ligands. This interaction is called superexchange.[16] In the hybrids this intermediate ligand is a halide anion. The magnetic d-orbitals on the metal centers both have electronic overlap with a filled p-orbital on the chlorine, as is schematically drawn in figure 2.6.

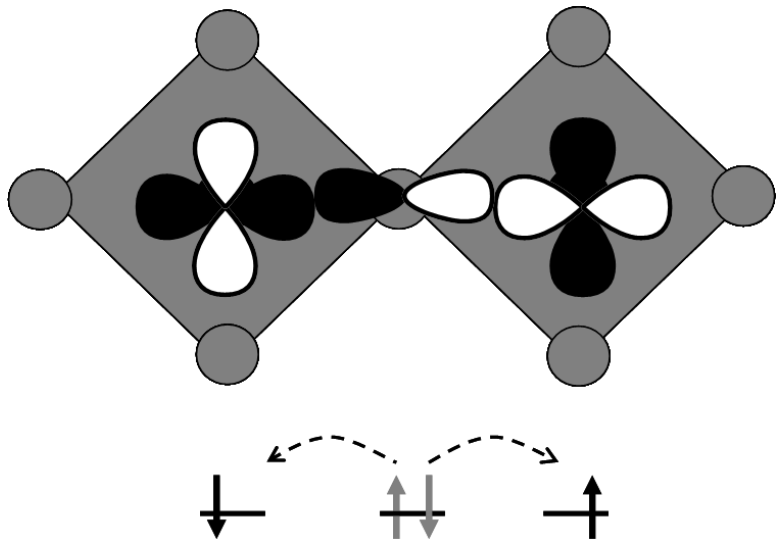

Figure 2.6: The magnetic superexchange interaction between two magnetic ions. The superexchange is an indirect magnetic interaction that is mediated by the non-magnetic chlorine ion (middle). The magnetic d-orbitals of the transition metal ions (the clover shaped orbitals located on the metal ions) overlap with the p-orbital of the chlorine atom (the dumbbell in the middle). Due to the Pauli principle and antisymmetrization of the orbitals this overlap results in an antiferromagnetic interaction between the magnetic spins.

The sign of this interaction depends on the metal-ligand-metal angle and the number of electrons in the d-orbitals of each magnetic ion. For identical magnetic ions and an angle of 180°, the interaction is antiferromagnetic.

2.1.3 Electric Properties

The electrical conductivity, σ, of a material is given by the expression:

$$\sigma = \frac{1}{\rho} = n\mu e \qquad (2.4)$$

In which ρ is the electrical resistivity, n is the number of carriers, μ is the electric mobility and e is the charge of the carrier. Just like the magnetic properties, the electric properties have to do with the occupation of the different orbitals. In a lattice, the orbitals of different atoms overlap and chemical bonds are created. This

overlap results in the creation of new electronic energy levels located in energy bands.[17] As a solid consists of many atoms, many new collective energy levels are created. The spacing between these energy levels is so small that they can be regarded as a continuous energy bands. Such energy bands are often characterized by the density of states (DOS) versus the energy, as is shown in figure 2.7. This figure shows the density of states for both an insulator and a metal. The density of states is the same in both figures; the only difference is the filling of the bands. The energy level, up to which the bands are filled with electrons, is called the Fermi energy, E_F. In the left figure, the lower band is completely filled with electrons and the upper band is completely empty. In the lower band, the valence band, all levels are filled. The conductivity relates to the availability of carriers and the possibility of those carriers to move to another (empty) state.

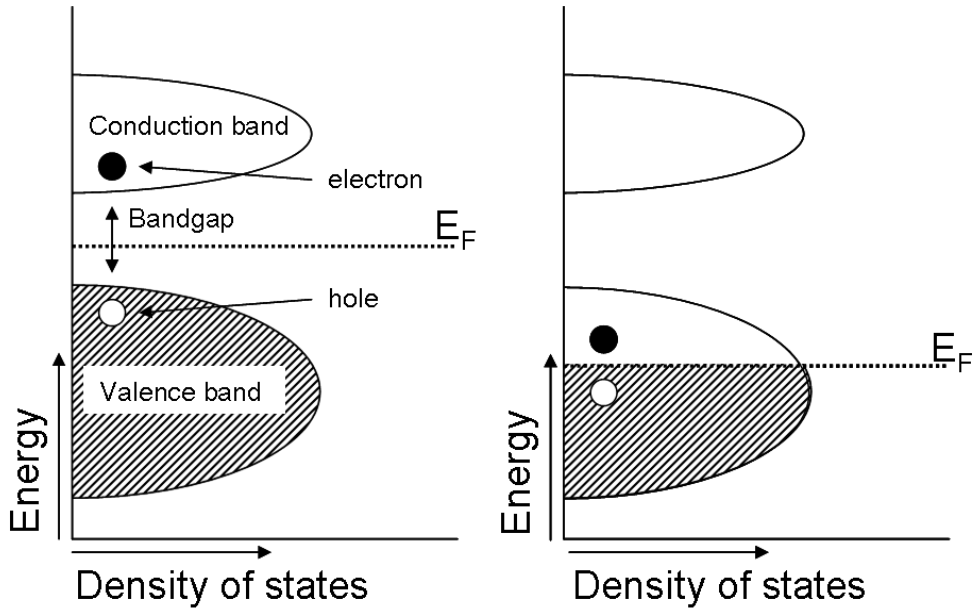

Figure 2.7: The electronic density of states versus the energy in an insulator (left) and a metal (right). The electronic levels are filled with electrons up to the Fermi level, E_F. For the insulator, E_F lies in the middle of the bandgap and the electrons have to overcome this bandgap to get in the conduction band. For metals, E_F lies in the band and the electrons can move without overcoming any barrier.

In case of the insulator at T=0K the Fermi level lies between the valence and the conduction band; there is a large energy gap between the available carriers (in the valence band) and the empty states in the conduction band. The carriers cannot overcome the energy barrier to reach the conduction band. Thus the carriers can not contribute to the conductivity and the material is insulating. At T≠0K the carriers do not longer occupy only the lowest available energy states. Instead the probability that a state with energy, E, is occupied at temperature T is given by the Fermi-Dirac distribution:

$$f(E) = [e^{\frac{(E-E_F)}{k_B T}} + 1]^{-1} \qquad (2.5)$$

Thus, at elevated temperatures some electrons are present in the conduction band. If an electron goes from the valance band to the conduction band, it will leave behind a vacant position in the valence band. This vacancy is called a hole and can be regarded as a particle with opposite charge as the electron. The hole in the valence band will contribute to the conductivity in the same way as the electron in the conduction band. The number of carriers depends on the temperature via:

$$n = Ce^{\frac{-Ea}{2k_B T}} \qquad (2.6)$$

Here, C is a constant depending on the total number of carriers, Ea is the activation energy, k_b is the Boltzmann constant and T is the temperature. A semiconductor is an insulator with a relatively small bandgap, in which carriers can be generated by temperature or doping. Both insulators and semiconductors will show an increase in the conductivity when the temperature is increased.

The DOS of a metal is shown in the right panel of figure 2.7. The Fermi level is located in the lower band. In this partially filled band, there is no energy gap between the carriers (electrons and holes) and the available energy states. Therefore the caries can freely move around and electrical transport can take place even at T= 0K. The number of carriers is not influenced by the temperature and metals will show a decrease of the conductivity upon increasing temperature, as

the thermal energy results in more scattering of the carriers by lattice excitations (phonons). The collisions with phonons will reduce the carrier mobility with increasing temperature.

2.2 Organic Electronics

Organic materials are used in applications in which versatile, easy processable and flexible materials are required, such as in plastics and dyes. Most organic materials are electrical insulators. Therefore, initially the main application of organic materials in electronics was as an insulator, for example to isolate the conduction wires that transport electricity from the socket to your coffee machine. Only recently, organic materials are more and more used as conductors,[18] ferroelectrics[19] and semiconductors[20] in electronic applications. These organic materials are mostly utilized in novel electronic devices, such as flexible displays[21] and OLEDs[23] (see figure 2.8). Organic materials can also be magnetic, but this property is hardly used in applications as magnetic organic materials are chemically reactive.[24]

Figure 2.8: Two applications of organic materials in electronic devices. The left picture shows a flexible display[21] and the right picture shows three different Organic Light Emitting Diodes (OLEDs).[22]

2.2.1 Molecules: Covalent Organic Architectures

Organic materials can, just like the inorganic materials, form lattices. For example, diamond and graphite are actually two different lattices of carbon atoms. In this section, however, the focus is on the properties of molecular organic materials. The "organic elements" form bonds in which 2 electrons are shared between atoms. Those are called covalent bonds. A molecule is a finite cluster of (carbon) atoms that are connected via such covalent bonds. Carbon atoms can have single, double and triple bonds. Such bonds are represented in figure 2.9.

The black spheres denote the carbon atoms and the white spheres denote the hydrogen atoms. Each carbon atom can make 4 bonds, thus when a carbon forms a double bond with a neighboring carbon atom it has only two positions available to bind hydrogen atoms. Molecules are often represented by abstract line drawings that are called bond-line structures.[25] In figure 2.9 this bond-line notation as well as the ball and stick model is used to describe molecules.

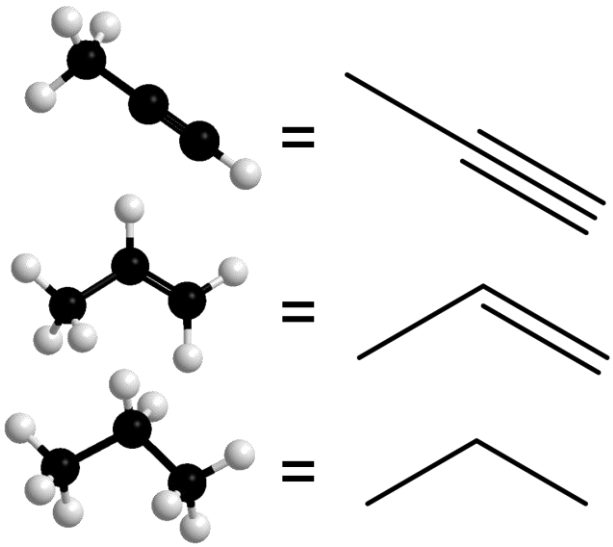

Figure 2.9: Organic molecules based on 3 carbon atoms, with a triple (upper), double (middle), and single (lower) bond. The black spheres denote the carbon atoms and the white spheres are the hydrogen atoms. Every carbon can make 4 bonds; thus if the carbon is connected to another carbon with a triple bond, only one bond is left for hydrogen. On the right side of the ball and stick pictures, the same molecules are drawn as skeletal structures.

The organic materials can be subdivided into two groups: the small molecules and the polymers. Polymers are very long chains of repeating units of covalently bound organic molecules (monomers). They form solids in which the large molecules are disordered, like in spaghetti. This thesis deals with the other class: the small molecules. These can, just like atoms, form well ordered crystals. Within the crystal, the molecules are connected to each other by van de Waals interactions or hydrogen bonds. An example of a pentacene crystal structure is shown in figure 2.11.

2.2.2 Electronic Properties of Organic Materials

In general, the electrical conductivity in organic materials is very low. This is, in the first place, due to the fact that the electrons are localized in the covalent bonds. However, in the last 50 years organic metals,[18] superconductors,[26] photoconductors[27] and semiconductors[20] have been developed.

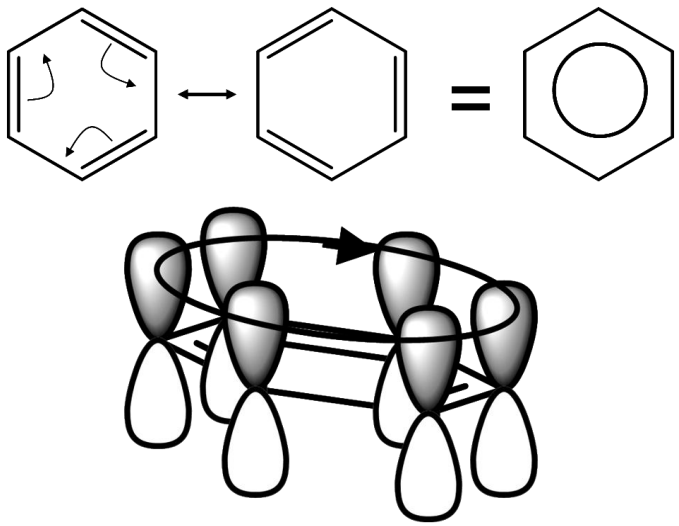

Figure 2.10: The top view and the side view of a benzene ring. (upper) The skeletal drawing of the benzene rings show 6 carbon atoms that are connected via alternating single and double bonds. However, all six bonds have the same length and the binding electrons are homogeneously delocalized over the p-orbitals of the carbon atoms (lower picture). This delocalized cloud of p-electrons is often referred to as a conjugated π-system.

A key ingredient for the electrical transport in organic materials is the delocalization of electrons within the molecule. This occurs when double and single carbon-carbon bonds are alternated in an organic chain or ring system. Those systems can be drawn in two different ways, see figure 2.10. Actually the situation is in between the two extremes drawn in 2.10. The bonds all have the same lengths and the electrons are delocalized over the network of p-orbitals (the π-system) within the molecule. This conjugated system allows the electrons to be transported from one end to the other end of the molecule.

To obtain electronic transport also the transportation of carriers between the different molecules is necessary. This can occur when the organic molecules are arranged such that the conjugated π-systems overlap. For ring systems, the overlap is optimal when they are oriented parallel, facing each other, at an inter-ring distance < 3.6 Å. Examples of good organic (semi-) conductors and their crystal structures are given in figure 2.11.

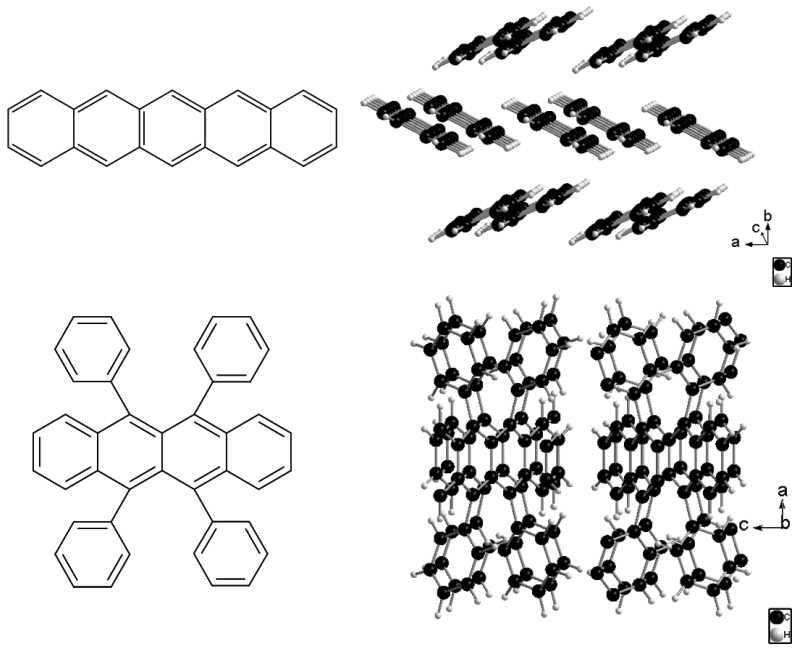

Figure 2.11: The pentacene (upper) and the rubrene (lower) molecules and their crystal structures. The pentacene molecule is flat and consists of 5 conjugated rings. The molecules arrange in the herringbone structure.[28] The rubrene molecule is not flat. It consists of a conjugated system of 4 rings, to which 4 extra phenyl rings are attached. In the crystal the molecules pack in dense 2-dimensional layers.[29]

In some organic co-crystals charge-transfer can occur between the different types of organic moieties. These materials can have excellent conductivity and sometimes even behave like a metal. An example of such an organic metal is TTF-TCNQ.[18]

In organic molecular materials without charge transfer, the interaction between the organic molecules is due to the relatively weak van der Waals bonds. The electronic structure of these materials is characterized by narrow bandwidths, which limits the mobility. Metallicity is not likely to occur, as the limited electron overlap also results in either completely filled or completely empty bands. Besides, the carriers are often trapped by the impurities and defects in the crystal.[30] As a result, the band model (that was described for the inorganic materials in the previous section) seldom applies to van der Waals bounded organic semiconductors. In general, the conductivity in the organic materials is better described by hopping: The charge transport occurs by the hopping of carriers from one to another localized state. In some cases, this hopping can be assisted by the vibrations of the lattice, due to which the charge mobility increases with temperature. The details of this hopping depend on the material and a general theory is still being developed.[31-33]

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